

Final Report

**NASA Grant NAGW-1292
Tunable Far Infrared Studies in Support of Stratospheric Measurements**

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1 Introduction

This report summarizes research done under NASA Grant NAGW-1292 from June 1, 1988 through September 30, 1997. The research performed during this reporting period has been a collaboration between institutions including the Smithsonian Astrophysical Observatory, the National Institute of Standards and Technology, the University of Oregon, and the NASA Langley Research Center.

The program has included fully line-resolved measurements of submillimeter and far infrared spectroscopic line parameters (pressure broadening coefficients and their temperature dependences, and line positions) for the analysis of field measurements of stratospheric constituents, far infrared database improvements, and studies for improved satellite measurements of the Earth's atmosphere. This research program is designed to enable the full utilization of spectra obtained in far infrared/submillimeter field measurements, such as FIRS-2, FILOS, IBEX, SLS, EosMLS, and proposed NASA and European Space Agency measurements of ClO and OH (*e.g.*, PIRAMHYD) for the retrieval of accurate stratospheric altitude profiles of key trace gases involved in ozone layer photochemistry.

For the analysis of the spectra obtained in the stratosphere from far infrared measurements it is necessary to have accurate values of the molecular parameters (line positions, strengths, and

pressure broadening coefficients) for the measured molecules and for possible interfering species. Knowledge of line positions is in increasingly good shape, with some notable exceptions. The increase in position information includes research that has been performed in the present program of research on HO₂, H₂O, H₂O₂, O₃, HCl, HF, HBr, HI, CO, OH, and ClO. Examples where further line position studies are necessary include hot band and minor isotopomer lines of some of the major trace species (H₂O, O₃) and normal lines of some triatomic and larger molecules (NO₂). Knowledge of strengths is in generally good shape, since most of the lines are from electric dipole transitions whose intensities are well determined from Stark effect measurements; exceptions include some molecules with large vibration-rotation interactions (NO₂) and internal motions (H₂O₂ above the lowest torsional state). The line parameters that are still the least well determined are pressure broadening coefficients, and their temperature coefficients. These are strongly dependent on the quantum states involved in the transitions, in a way that is much more complex than the simple projection by directional cosine matrix elements involved in determination of rotational line strengths from static dipole moments.

The following molecules have now been measured or detected in the atmosphere using far infrared and millimeter-wave emission spectroscopy from balloon- and satellite-borne spectrometers: OH, HO₂, H₂O (including minor isotopomers and hot band lines), H₂O₂, O³P, O₂ (including minor isotopomers), O₃ (including minor isotopomers and hot band lines), HOCl, HCl, HF, HBr, ClO, CO, CO₂, N₂O, NO₂, N₂O₅, HNO₃, ClNO₃, and HCN. Many of these species have spectral lines that are saturated in stratospheric spectra. In these cases, the measured line equivalent widths are proportional to (line strength × Lorentz width)^{1/2} so that the pressure broadening coefficients are as important as the line intensities in determining concentration profiles. Interpretation of field measurements for these species have required ongoing measurement programs of pressure broadening measurements. Other species (HO₂, HOCl, H₂O₂, HBr, and NO₂, as examples) have required further line position studies in order to fully analyze the field measurements.

2 Developmental Work

In the TuFIR technique, tunable far infrared radiation is generated by means of CO₂ laser difference frequencies in a metal-insulator-metal (MIM) diode [1, 2, 3]. This NIST-developed technique has been demonstrated to be an excellent source of coherent radiation for spectroscopy. As summarized in reference 2, the technique has been used to measure highly accurate far infrared frequencies of stable molecules to serve as frequency and wavelength calibration standards, and to measure frequencies of transient species for astronomical searches. The general features of the TuFIR technique are summarized here. In the usual two-wave mixing mode of TuFIR operation, radiation from two CO₂ lasers is combined on a beam splitter and then focussed on a MIM diode, where the difference frequency (far infrared) radiation is generated. One laser is

a CO₂ waveguide laser, frequency-offset locked to a saturated fluorescence stabilized CO₂ laser. The second laser is a frequency modulated, saturated fluorescence stabilized CO₂ laser. The FIR radiation is thus also frequency modulated. Phase sensitive detection is used to measure the modulation-broadened first derivative of the sample absorption. The waveguide CO₂ laser provides a tunability of up to ± 200 MHz. Acousto-optic modulators operating at 90 MHz are used to isolate the lasers from the MIM diode and to provide additional wavelength coverage. By changing pairs of CO₂ laser lines we can cover about 80% of the spectrum between 0.3 and 6 THz. The FIR frequency is known absolutely to ± 10 KHz [4] and has a spectral purity of ~ 10 KHz. An alternative method of TuFIR operation, three-wave mixing, trades off some of the FIR power for increased tunability. It is effected by directly mixing two saturated fluorescence stabilized CO₂ laser, along with a tunable microwave source, on the MIM diode. Either TuFIR mode is capable of providing fully-resolved measurements at the Doppler widths of far infrared lines, which range from about 0.5 to 20 MHz. The three-wave mixing method is now normally the preferable method of operation, since the choice of CO₂ lasing lines is much less constrained and since the power curve for the tuned FIR radiation is much flatter. Since lines can be fully resolved by the TuFIR method, linewidths can be measured directly, rather than being inferred from a curve of growth. The curve of growth method, necessary when the instrument resolution is coarser than the linewidth, requires that the amount of absorber gas be kept constant. This is a major difficulty when performing measurements on unstable species such as OH, or on strongly surface absorbing species such as HCl or HF.

We have now developed an expertise in ultra-high resolution spectroscopy using the TuFIR method that includes:

- The development of radical source chemistries, allowing us to measure pressure broadening and line positions of OH, HO₂ and ClO;
- Development of 3-wave mixing, which trades off some of the power available in the tunable far infrared beam for much wider tunability. For a particular measurement, either 2-wave or 3-wave mixing can be chosen according to experimental need;
- Design and fabrication of spectroscopy cells, a flow-metering system for radical chemistry, and other laboratory apparatus;
- Development of instrument control and data acquisition software, allowing for precise control of the TuFIR instrument parameters and long integration times for weak spectral lines and;
- Development of software for nonlinear least-squares fitting of measured spectra to obtain pressure broadening coefficients and/or line positions, based upon the algorithm of Marquardt [5]. Spectra which have the typical modulation-broadened Voigt derivative line

shape (other line shape options are available as well, including normal Voigt and Voigt second derivative) are calculated using a complete radiative transfer model, including the effects of line saturation and modulation broadening. Voigt line profiles and their derivatives are calculated, with the capability of varying Doppler and Lorentz widths, line positions, absorber amounts, and baseline and laser power curve variations modeled with polynomials up to cubic order.

- Development of software to perform multiple linear regressions to obtain line broadening and/or shifting information from studies employing complex source chemistries.
- Development of Hamiltonian fitting capability that includes asymmetric top molecules with electron spin-rotation interactions, up to high degree in centrifugal distortion, and nuclear hyperfine (spin-spin dipolar, Fermi contact, and nuclear quadrupole) interactions.

3 Molecule Studies

We have developed a capability for performing spectroscopic measurements on radical species and on weak lines that is unique. Our laboratory measurements under this program include:

Spectral Standards TuFIR line position measurements of CO, HCl, and HF for use as spectral standards in the far infrared from 10-200 cm^{-1} have been determined.

OH Studies of the pressure broadening of the hyperfine-resolved lines at 118.455 cm^{-1} and 83.869 cm^{-1} by N_2 , O_2 , H_2 and He, and their temperature dependences have been completed and published. These studies include re-determination of the OH line positions to higher accuracy. It should be noted that the studies of the 83.869 and 118.455 cm^{-1} lines provide all of the necessary quantitative spectroscopic parameters needed for the analysis of OH data from the satellite-based OH measurements currently being proposed by NASA and ESA. The 118 cm^{-1} line is the best line of the 13 lines measured by FIRS-2 for stratospheric OH measurements. The 83 cm^{-1} line is the one usually considered for heterodyne measurements of OH because of the somewhat lower frequency and the availability of a suitable far infrared laser line of CH_3OH to use as a local oscillator. The studies of OH have also led to the development of OHIO (OH Interferometer Observations), a proposed satellite-based instrument that could measure stratospheric OH using a combination of a single Fabry-Perot resonator and a diffraction grating, with a detector operated at 80 K. This concept is being pursued in collaboration with the Space Research Organization of the Netherlands as a potential OH measurement device for both NASA and ESA satellite platforms, and was a component of the ESA PIRAMHYD study (OH profiling by far infrared limb sounding).

- HO₂** The positions of a number of HO₂ lines have been determined, including all but one of the lines used for remote sensing in the far infrared by the SAO, and three of the six lines used by IROE. The measured lines have been included in the 1992 SAO line parameter database. A new program has been written to fit the measured lines to a Hamiltonian expression including spin-rotation and hyperfine interactions by full diagonalization in a parity-conserving basis set. The analysis of the measured spectrum, simultaneously fitted with previous microwave, millimeter and submillimeter spectra [6, 7], has been completed and published. The pressure broadening of the HO₂ doublet 13_{2,12} — 12_{1,11}, $J = 27/2 \leftarrow 25/2$ at 83.32 cm⁻¹ by N₂ and O₂ at room temperature was measured in collaboration with the European Laboratory for Nonlinear Spectroscopy (LENS), in support of potential future heterodyne measurements in the atmosphere. The results from this investigation have now been published. Further work to extend the Hamiltonian fitting to higher values of K_a (up to 9) and N (up to 31) by combining the simultaneous fitting with combination differences from near infrared measurements of the lowest electronic transition has been completed and published. This research was done in collaboration with the Steacie Institute for Molecular Sciences, National Research Council of Canada, and the University of Ulm.
- HCl** Measurements of pressure broadening of the 83.39 cm⁻¹ R₃ line of H³⁵Cl, including its temperature dependence, have been published.
- HI** We have measured and analyzed the quadrupole-resolved rotational spectrum of HI up to the R₁₁ lines. HI is of general spectroscopic interest, particularly since it provides a good example of the rotational dependence of the nuclear quadrupole coupling. In combination with measurements of the vibrational dependence, the data are used to determine the electric field gradient at the ¹²⁷I nucleus and its first two derivatives with respect to the internuclear distance. The measurements also provide an accurate value of the ¹²⁷I nuclear spin-rotation interaction.
- O₂** Pressure broadening of the 50.87, 60.46, and 83.47 cm⁻¹ lines of O₂ has been published. We have published a critical study on the use of O₂ magnetic dipole-allowed rotation lines for the calibration of far infrared atmospheric measurements.
- H₂O** The N₂ and O₂ broadening coefficients, and their temperature dependences over the 200-300 K range, of the H₂O line at 88.650 cm⁻¹ have been determined.
- O₃** The N₂ and O₂ broadening coefficients, and their temperature dependences over the 200-300 K range, of the O₃ line at 114.469 cm⁻¹ have been determined.
- H₂O₂** Detailed positions have been determined for most of lines which are major contributors to the ^RQ₄ and ^RQ₅ branches of the lowest torsional band, *i.e.*, the structures which are

currently used for atmospheric H₂O₂ measurements.

HF Temperature-dependent studies of the N₂ and O₂ broadening of the HF R₃ line at 164 cm⁻¹, used by FIRS-2 and other instruments for stratospheric HF monitoring, have been completed. The data have been analyzed and a publication is currently in preparation. The study also includes a more accurate determination of the line position.

1992 Smithsonian Astrophysical Observatory Line Parameter Database

The Smithsonian Astrophysical Observatory maintains a line parameter listing for analysis of atmospheric thermal emission measurements in the far- and mid-infrared which is updated at frequent intervals. The current version of the listing extends from 10-800 cm⁻¹, and contains more than 150,000 lines. The listing is modeled on the HITRAN line parameter listing [8], and contains the best currently available parameters from the HITRAN listing, the JPL Microwave and Submillimeter Line Listing [9], laboratory measurements (including those made under the present research program), and extensive library research and calculations. The SAO line parameter listing reflects the fact that we have thoroughly researched every line of every molecule used in SAO atmospheric measurements and continue to improve the database as atmospheric measurements require. SAO92 contains, in particular, the line parameters that have enabled recent stratospheric measurements of HO₂ [10, 11, 12], H₂O₂ [11, 12, 13], HOCl [12, 14], and the first measurement of stratospheric HBr [15] to be made. A publication on the database has appeared in the Journal of Quantitative Spectroscopy and Radiative Transfer [16]. The database is updated regularly, and is available at <http://firs-www.harvard.edu/www/sao92.html>.

4 Publications from this Research Program

Laboratory Measurement of the Rotational Spectrum of the OH Radical with Tunable Far-Infrared Radiation, J.M. Brown, L.R. Zink, D.A. Jennings, K.M. Evenson, A. Hinz, and I.G. Nolt, *Astrophys. J.* 307, 410-413 (1986).

The Microwave and Far-Infrared Spectra of the ¹⁸OH Radical, E.R. Comben, J.M. Brown, T.C. Steimle, K.R. Leopold, and K.M. Evenson, *Astrophys. J.* 305, 513-517 (1986).

The Far-Infrared Laser Magnetic Resonance Spectrum of the ¹⁷OH Radical: Determination of Nuclear Hyperfine Parameters, K.R. Leopold, K.M. Evenson, E.R. Comben, and J.M. Brown, *J. Molec. Spectrosc.* 122, 440-454 (1987).

High Resolution Spectroscopy of HF from 40 to 1100 Wavenumbers: Highly Accurate Rotational Constants, D.A. Jennings, K.M. Evenson, L.R. Zink, C. Demuynck, J.C. Destombes, and B. Lemoine, *J. Molec. Spectrosc.* **122**, 477-480 (1987).

Stark Spectroscopy Using Tunable Far-Infrared Radiation, L.R. Zink, D.A. Jennings, K.M. Evenson, A. Sasso, and M. Inguscio, *J. Opt. Soc. Am. B* **4**, 1173-1176 (1987).

Sub-Doppler Tunable Far-Infrared Spectroscopy, M. Inguscio, L.R. Zink, K.M. Evenson, and D.A. Jennings, *Opt. Lett.* **12**, 867-869 (1987).

Accurate Rotational Constants of CO, HCl and HF: Spectral Standards for the 0.3 to 6 THz (10 to 200 cm^{-1}) Region, I.G. Nolt, J.V. Radostitz, G. Di Lonardo, K.M. Evenson, D.A. Jennings, K.R. Leopold, M.D. Vanek, L.R. Zink, A. Hinz, and K.V. Chance, *J. Molec. Spectrosc.* **125**, 274-287 (1987).

Air- and Oxygen-broadening Coefficients for the O_2 Rotational Line at 60.46 cm^{-1} , D.A. Jennings, K.M. Evenson, M.D. Vanek, I.G. Nolt, J. V. Radostitz, and K.V. Chance, *Geophys. Res. Lett.* **14**, 722 (1987); erratum *Geophys. Res. Lett.* **14**, 981 (1987).

Coherent Tunable Far Infrared Radiation, D.A. Jennings, *Appl. Phys. B* **48**, 311-313 (1989).

Atomic Oxygen Fine-Structure Splittings with Tunable Far-Infrared Spectroscopy, L.R. Zink, K.M. Evenson, F. Matsushima, T. Nelis, and R.L. Robinson, *Astrophys. J.* **371**, L85 (1991).

Pressure Broadening of the 118.455 cm^{-1} Rotational Lines of OH by H_2 , He, N_2 , and O_2 , K.V. Chance, D.A. Jennings, K.M. Evenson, M.D. Vanek, I.G. Nolt, J.V. Radostitz, and K. Park, *J. Molec. Spectrosc.* **146**, 375-380 (1991).

Pressure Broadening of the 2.5 THz H^{35}Cl Rotational Line by N_2 and O_2 , K. Park, K.V. Chance, I.G. Nolt, J.V. Radostitz, M.D. Vanek, D.A. Jennings, and K.M. Evenson, *J. Molec. Spectrosc.* **147**, 521-525 (1991).

On the Use of O_2 Spin-Rotation Lines for Elevation Angle Calibration of Atmospheric Thermal Emission Spectra, K.V. Chance, W.A. Traub, K.W. Jucks, and D.G. Johnson, *Int. J. IR MM Waves* **12**, 581-588 (1991).

Accurate Far-Infrared Rotational Frequencies of Carbon Monoxide, T.D. Varberg and K.M. Evenson, *Astrophys. J.* **385**, 763-765 (1992).

The Far Infrared Spectrum of HI, K.V. Chance, T.D. Varberg, K. Park, and L.R. Zink, *J. Molec. Spectrosc.* **162**, 120-126 (1993).

Pressure Broadening of the 2.4978 THz Rotational Lines of HO_2 by N_2 and O_2 , K. Chance, P. De Natale, M. Bellini, M. Inguscio, G. Di Lonardo and L. Fusina, *J. Molec. Spectrosc.* **163**,

67-70 (1994).

The OHIO Concept: A Baseline Design for Satellite-Based Measurements of Stratospheric OH, K. Chance, J.J. Wijnbergen, W. Schneider, and J.P. Burrows *Proc. S.P.I.E., High-Temperature Superconducting Detectors: Bolometric and Nonbolometric*, 2159, 21-33 (1994).

The Smithsonian Astrophysical Observatory Database SAO92, K. Chance, K.W. Jucks, D.G. Johnson, and W.A. Traub, *J. Quant. Spectrosc. Radiat. Transfer* 52, 447-457 (1994).

The OHIO Concept: Refinements on a Design for Satellite-Based Measurements of Stratospheric OH, K. Chance, J.J. Wijnbergen, P. de Valk, W. Schneider, and J.P. Burrows, *Proc. S.P.I.E., Atmospheric Sensing and Modelling*, 2311, 236-239 (1994).

OH Measurements with Airborne and Satellite Instrumentation in the Lower and Upper Stratosphere, J.P.J.M.M. de Valk, J.J. Wijnbergen, K. Chance, J.P. Burrows, and W. Schneider, *Proc. S.P.I.E., Passive Infrared Remote Sensing of Clouds and the Atmosphere II*, 2309, 279-286 (1994).

The Far Infrared Fabry-Perot Spectrometer as a Satellite-Based Atmospheric Limb Sounder, J. Wijnbergen, J. P. Burrows, K. Chance, W. Schneider, and P. de Valk, *Proc. S.P.I.E., Passive Infrared Remote Sensing of Clouds and the Atmosphere II*, 2309, 287-294 (1994).

LENS Group Contribution to ISORAC I, M. Bellini, P. De Natale, M. Inguscio, M. Prevedelli, G. Di Lonardo, L. Fusina, G. Buffa, O. Tarrini, and K. Chance, *CEC Air Pollution Research Report 52: Infrared Spectroscopy of Ozone and Related Atmospheric Constituents*, ed. D. Hausamann and J.-M. Flaud, 66-74, ISBN 92-826-8213-7 (1994).

Fabry-Pérot Spectrometer Concept for Satellite Based Atmospheric Observations in the Far Infrared, J. J. Wijnbergen, J. P. Burrows, K. Chance, W. Schneider, and A. R. W. de Jonge, *International Symposium on SPACE OPTICS*, Europto series (1994).

Far Infrared Spectrum of HO₂, K. V. Chance, K. Park, K. M. Evenson, L. R. Zink, and F. Stroth, *Journal of Molecular Spectroscopy* 172, 407-420 (1995).

Pressure Broadening of the 83.869 cm⁻¹ Rotational Lines of OH by N₂, O₂, H₂, and He, K. Park, L.R. Zink, K.M. Evenson, K.V. Chance, and I.G. Nolt, *Journal of Quantitative Spectroscopy and Radiative Transfer* 55, 285-287 (1996).

Pressure Broadening of the 50.873 cm⁻¹ and the 83.469 cm⁻¹ Molecular Oxygen Lines, K. Park, I.G. Nolt, T.C. Steele, L.R. Zink, K.M. Evenson, K.V. Chance, and A.G. Murray, *Journal of Quantitative Spectroscopy and Radiative Transfer* 56, 315-316 (1996).

THz Applications in Atmospheric Sensing, K. Chance, in "Metrology Issues in Terahertz Physics and Technology," pp. 63-85, NIST special publication (1996).

Pressure Broadening of Far Infrared Rotational Transitions: 88.65 cm^{-1} H_2O and 114.47 cm^{-1} O_3 , K.V. Chance, K. Park, and K.M. Evenson, in preparation.

Molecular Constants for the Ground State of HO_2 , K.V. Chance, K. Park, K.M. Evenson, L.R. Zink, F. Stroh, E.H. Fink, and D.A. Ramsay, *Journal of Molecular Spectroscopy* 183, 418 (1997).

5 References

- 1 Tunable Far-infrared Spectroscopy, K. M. Evenson, D. A. Jennings, and F. R. Petersen, *Appl. Phys. Lett.* 44, 576-578 (1984).
- 2 K. M. Evenson, D. A. Jennings, K. R. Leopold, and L. R. Zink, in "Laser Spectroscopy VII", T. W. Haensch and Y. R. Shen Eds. *Springer Series in Optical Sciences* 49, 366, New York (1985).
- 3 K. M. Evenson, D. A. Jennings, L. R. Zink, and K. R. Leopold, Tunable Far Infrared Spectroscopy, Digest 11th International Conference on Infrared and Millimeter Waves, G. Moruzzi Ed. 267-271 (1986).
- 4 Accurate Far-infrared Rotational Frequencies of Carbon Monoxide, T. D. Varberg and K. M. Evenson, *Astrophysical Journal Letters* 385 763-765 (1992).
- 5 An Algorithm for Least-squares Estimation of Non-linear Parameters, D. L. Marquardt, *J. Soc. Indust. Appl. Math.* 2, 431-441 (1963).
- 6 Microwave Spectrum of the HO_2 Radical, S. Saito, *J. Molec. Spectrosc.* 65, 229-238 (1977)
- 7 The Millimeter and Submillimeter Spectrum of HO_2 : The Effects of Unpaired Electron Spin in a Light Symmetric Rotor, A. Charo and F.C. De Lucia, *J. Molec. Spectrosc.* 94, 426-436 (1982)
- 8 The HITRAN Molecular Database Editions of 1991 and 1992, L. S. Rothman, R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. Chris Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown, and R. A. Toth, *J. Quant. Spectrosc. Radiat. Transfer* 48, 469-507 (1992).
- 9 Submillimeter, Millimeter, and Microwave Spectral Line Catalog, R. L. Poynter and H. M. Pickett, *Publ. 80-23, revision 2*, Jet Propulsion Laboratory, Pasadena, CA, 1984; current values obtained by FTP.
- 10 Stratospheric Hydroperoxyl Measurements, W. A. Traub, D. G. Johnson, and K. V. Chance, *Science* 247, 446-449 (1990).

- 11 Spectroscopic Measurement of HO₂, H₂O₂, and OH in the Stratosphere, J. H. Park and B. Carli, *Journal of Geophysical Research* 96, 22,535-22,541 (1991).
- 12 Simultaneous Measurements of Stratospheric HO_x, NO_x, and Cl_x: Comparison with a Photochemical Model, K. Chance, W.A. Traub, D.G. Johnson, K.W. Jucks, P. Ciarpallini, R.A. Stachnik, R.J. Salawitch, and H.A. Michelsen, *Journal of Geophysical Research* 101, 9031-9043 (1996).
- 13 Measurement of the Stratospheric Hydrogen Peroxide Concentration Profile Using Far Infrared Thermal Emission Spectroscopy, K. V. Chance, D. G. Johnson, W. A. Traub, and K. W. Jucks, *Geophysical Research Letters* 18, 1003-1006 (1991).
- 14 Measurement of Stratospheric HOCl: Concentration Profiles, Including Diurnal Variation, K. V. Chance, D. G. Johnson, and W. A. Traub, *Journal of Geophysical Research* 94, 11,059-11,069 (1989).
- 15 Detection of HBr and Upper Limit for HOBr: Bromine Partitioning in the Stratosphere, D. G. Johnson, W. A. Traub, K. V. Chance, and K. W. Jucks, *Geophysical Research Letters* 22, 1373-1376 (1995).
- 16 The Smithsonian Astrophysical Observatory Database SAO92, K. Chance, K. W. Jucks, D. G. Johnson, and W. A. Traub, *Journal of Quantitative Spectroscopy and Radiative Transfer* 52, 447-457 (1994).